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Recovery of Tungsten From a Hydrothermally Altered Deposit

By A. E. Raddatz, J. M. Gomes,
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UNITED STATES DEPARTMENT OF THE INTERIOR
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RECOVERY OF TUNGSTEN FROM A HYDROTHERMALLY ALTERED DEPOSIT

By A. E. Raddatz,[1] J. M. Gomes,[2] J. J. Sjoberg,[3] and M. M. Wong[4]

ABSTRACT

The Bureau of Mines is investigating methods for recovering tungsten from domestic resources. A calcine-quench-leach (CQL) technique was developed for the extraction of tungsten from the Golconda, Nev., hot springs ores. The deposit contains disseminated tungsten that cannot be beneficiated by conventional techniques and must be treated by hydrometallurgical methods.

The CQL procedure consists of calcining the ore at 900° C for 3 hours, quenching in a solution containing 1.5 parts of Na_2CO_3 and 1.5 parts of NaOH per part of WO_3 in the ore and at a solution-to-ore ratio of 3 to 1, leaching at 200° C and at 250 psig for 3 hours, and filtering and washing the residue. A series of closed-circuit batch tests showed that 92 pct of the tungsten was extracted from a sample containing 2.32 wt-pct WO_3. The pregnant solution contained 11 g/l WO_3.

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INTRODUCTION

The Bureau of Mines is concerned with the development of efficient extraction technologies for domestic mineral resources. Unless economic methods to utilize domestic materials are developed, more tungsten will have to be imported (9).[5] The Golconda tungsten deposit is an identified resource that can be easily mined.

The deposit, which is 3 miles east of Golconda, Nev., in the foothills of the Edna Mountains, is a hot springs deposit occurring in blanketlike masses under beds of calcareous tufa. The ore contains 0.5 to 7 wt-pct WO_3. The tungsten is disseminated throughout colloidal, hydrated iron and manganese oxides. No common tungsten minerals such as scheelite and wolframite have been identified in the ore. The deposit was described by Kerr and Penrose (3, 8). The deposit is estimated to contain 500,000 short ton units of WO_3 (6).

Since the tungsten cannot be concentrated by any conventional beneficiation process, the ores must be treated directly. The Nevada-Massachusetts Mining Co. built a mill in Golconda to treat the ore by a hydrometallurgical process and operated the property from 1942 to 1945 (2, 7). The ore was mixed with salt, soda ash, and coal and treated in a Dwight-Lloyd sintering machine. The sinter was ground and leached with hot water. The sodium tungstate that formed during sintering was extracted. Calcium chloride subsequently was added to the clarified pregnant solution to precipitate the tungsten as synthetic scheelite. Tungsten recovery was 60 to 70 pct of the WO_3 in the ore.

The objective of the Bureau's research in this area was to develop a technique for extracting more than 90 pct of the tungsten from the Golconda hot springs ore.

DESCRIPTION OF SAMPLES

In earlier mining operations, the Golconda deposit was divided into several large, irregular areas. From east to west, the areas are Bed Springs Hill, Crib Shaft Hill, and Big Four. The analysis of five ore samples from the three areas are shown in table 1.

TABLE 1. - Analysis of samples, percent

Ore	Mine area	WO_3	Fe_2O_3	MnO_2	CaO	Al_2O_3	SiO_2	BaO
1	Crib Shaft.....	1.64	28.6	3.6	19.6	8.7	19.2	0.09
2	.....do.[1].....	1.60	28.7	19.0	8.5	5.0	3.4	.34
3	Bed Springs....	.68	37.3	.4	1.1	8.3	38.0	.51
4	Big Four.....	2.32	2.1	69.4	5.8	.5	3.1	3.48
5	.....do.....	.78	24.0	10.7	2.0	13.2	44.0	.16

[1]Ore contains 22 pct CaF_2.

Samples from the Golconda deposit had not been previously studied with a scanning electron microscope. Identification of the tungsten minerals and determination of tungsten association with other minerals would assist in selecting an extraction technique for the tungsten. Results of a mineralogical study of selected samples are given in the appendix, and indicate the following:

- There was not enough tungsten in any grain to show the presence of common tungsten minerals such as scheelite or wolframite.

[5]Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

- Tungsten occurred in grains with iron or manganese oxides or mixtures of the two oxides.
- Not all iron or manganese oxide grains contained tungsten.
- Manganese oxide grains containing tungsten also analyzed 4 to 9 pct Ba. Ferric oxide grains containing tungsten analyzed ≤0.6 pct Ba.
- Grains containing major quantities of calcium, either as limestone or fluorspar, contained ≤0.8 pct W.
- The highest tungsten content, 7.9 pct, was associated with a grain containing 43 pct Fe, 0.2 pct Mn, and 0.5 pct Ba.

Tungsten values in the hot springs ore cannot be beneficiated by an ore dressing technique. Because of the disseminated nature of the tungsten, the ore must be treated by a hydrometallurgical technique.

EXPERIMENTAL PROCEDURE

The CQL (calcine-quench-leach) procedure for extracting tungsten from Golconda hot springs ore was chosen for study after several conventional methods had been investigated. Pressure leaching in alkaline solutions at 200° C and 250 psig resulted in tungsten extractions of <30 pct. Calcining the ore at temperatures up to 900° C and leaching at 100° C and atmospheric pressure resulted in tungsten extraction of <50 pct. Calcining at 800° to 900° C and pressure leaching at 200° C and 200 to 300 psig resulted in an 86-pct-W extraction. Adding an alkaline quench increased tungsten extraction to 90 pct. The CQL processing sequence was selected for further study (1).

CQL Process

The laboratory procedure included (1) calcining the ground ore in a fireclay crucible for 2 to 3 hours at 800° to 900° C, (2) quenching the hot ore in an alkaline solution that was agitated in a large blender, (3) pressure leaching the slurry at 200° C and 200 to 300 psig for 2 to 3 hours, and (4) cooling and filtering the slurry. The residue was washed twice with an alkaline solution. A flowsheet for the CQL procedure is shown in figure 1.

The bench-scale leaching was performed in 2-liter Parr[6] autoclaves, and large-scale, 2-kg leaches were leached in a 2-gal autoclave manufactured by Autoclave Engineers, Inc. Technical-grade NaOH (sodium hydroxide) and Na_2CO_3 (sodium carbonate) were used in preparing the leaching solutions. Determinations of tungsten in solids and solutions were performed by an X-ray fluorescence procedure.

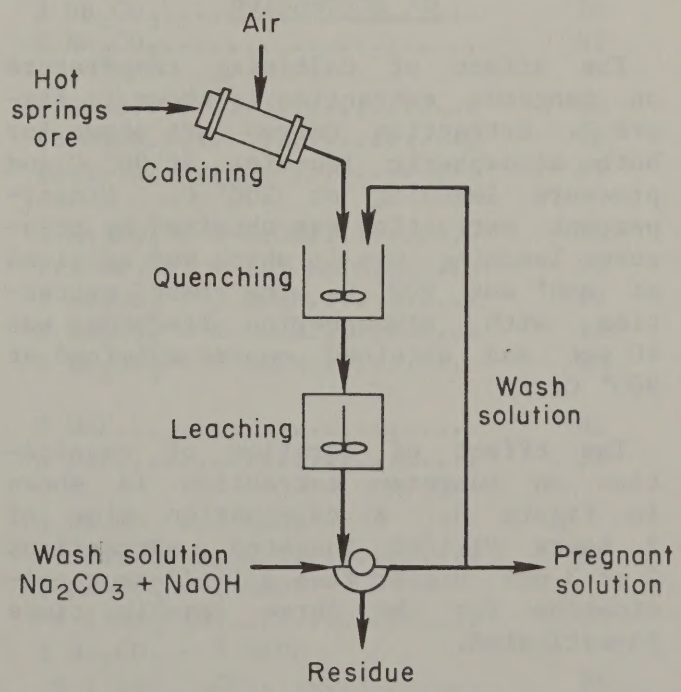

FIGURE 1. - Flowsheet for CQL (calcine-quench-leach) procedure.

[6]Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

Operating Conditions

The best operating conditions for the CQL process were as follows:

Calcining temperature	850° to 900° C.
Duration of calcination	2 to 3 hours.
$\frac{\text{Quench-leach solution}}{WO_3 \text{ in ore}}$, weight ratio	$\frac{1.5\ Na_2CO_3 + 1.5\ NaOH}{1.0\ WO_3}$.
Leaching solution:ore, weight ratio	2:1 to 3:1.
Leaching temperature	200° C.
Leaching pressure	250 to 400 psig.
Duration of leach	2 to 3 hours.
Residue washes	2 or 3, equal to leaching solution volume.

Unless noted otherwise, these operating conditions and laboratory procedures were used in all experiments.

EXPERIMENTAL RESULTS

Effects of Operating Conditions on Extraction

The effect of calcining temperature on tungsten extraction is shown in figure 2. Extraction curves are shown for both atmospheric leaching at 90° C and pressure leaching at 200° C. Ninety-percent extraction was obtained by pressure leaching ore 1, which was calcined at 850° and 900° C. The best extraction with atmospheric leaching was 40 pct and obtained on ore calcined at 900° C.

The effect of duration of calcination on tungsten extraction is shown in figure 3. A calcination time of 2 hours yielded tungsten extractions 2 or 3 pct higher than a 1-1/2-hour calcination for the three leaching times investigated.

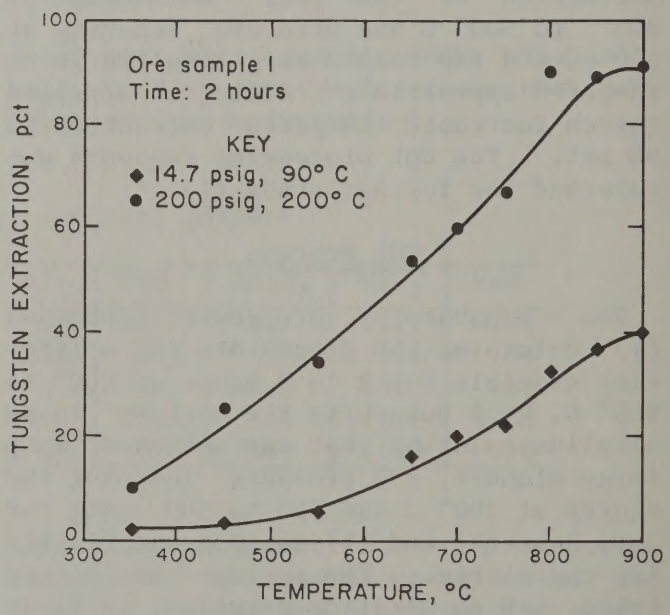

FIGURE 2. - Effect of calcining temperature on tungsten extraction.

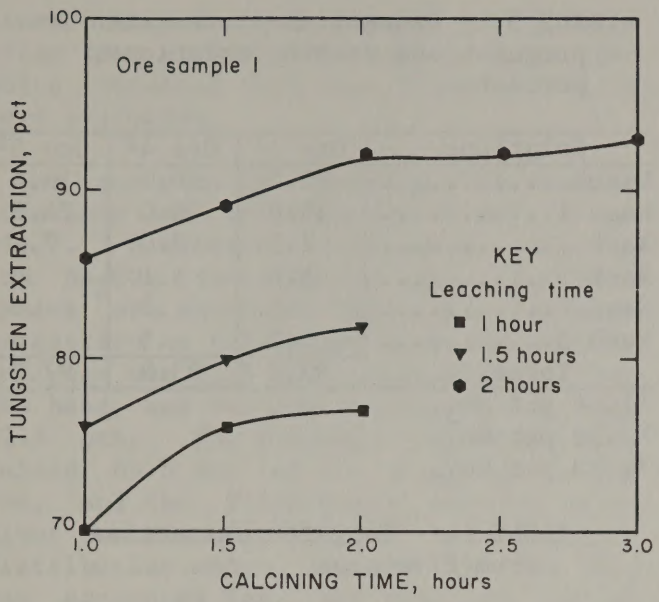

FIGURE 3. - Effect of duration of calcination on tungsten extraction at 900° C.

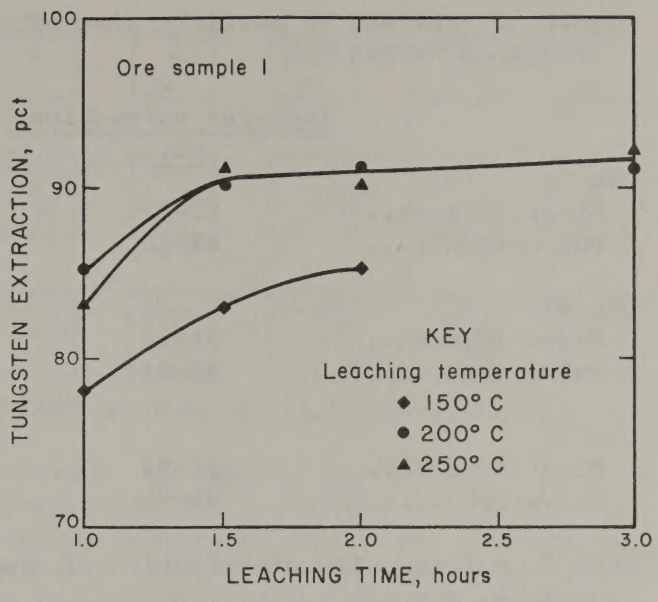

FIGURE 4. - Effect of duration of leach on tungsten extraction.

The effect of leaching reagents at different weight ratios on tungsten extraction is shown in table 2. Tungsten extractions from ore 1 were 90 pct or more when 6 parts of Na_2CO_3, 12 parts of NaOH, or mixtures of 1.5, 3, or 6 parts each of Na_2CO_3 and NaOH per part of WO_3 were used. The 1.5 Na_2CO_3 and 1.5 NaOH mixture was the least costly and was considered the best suite.

The effect of duration of the leaching process and temperature of the leaching solution on tungsten extraction is shown in figure 4. Extractions of more than 90 pct were obtained by leaching ore 1 for 2 hours at 200° C. The pressure ranged from 200 to 400 psig during the leaching. Pressure variations were due to the vapor pressure of CO_2 (carbon dioxide).

The effect of particle size on tungsten extraction from three ores is shown in table 3. The ore samples were crushed to minus 10 mesh, and one-half of the sample was pressure leached; the other half was pulverized and leached. Tungsten extractions near 90 pct were obtained with minus 10-mesh ore 1 and with both the minus 10-mesh and pulverized fractions of ores 4 and 5. Screen analyses of the minus 10-mesh and pulverized fractions of ore 4 are shown in table 4.

TABLE 2. - Effect of leaching reagents on tungsten extraction

Reagents (in ratio by weight to WO_3)	Tungsten extraction,[1] pct
2 Na_2CO_3	36
3 Na_2CO_3	74
6 Na_2CO_3	92
6 NaOH	60
12 NaOH	93
18 NaOH	89
1 Na_2CO_3 + 1 NaOH	70
1.5 Na_2CO_3 + 1.5 NaOH	90
3 Na_2CO_3 + 3 NaOH	92
6 Na_2CO_3 + 6 NaOH	92
9 Na_2CO_3 + 9 NaOH	89
2 NAF	46
4 NAF	52
3 Na_2CO_3 + 3 NaOH + 0.6 $Na_2B_4O_7$	87
3 Na_2CO_3 + 3 NaOH + 1 $Na_4P_2O_7$	95
3 Na_2CO_3 + 3 NaOH + 1 $(NH_4)_2CO_3$	94

[1]Based on analyses of head samples and residues.

TABLE 3. - Effect of particle size on tungsten extraction

	Tungsten extraction, pct
Ore 1:	
Minus 10 mesh..	87-92
Pulverized.....	84-88
Ore 4:	
Minus 10 mesh..	91-94
Pulverized.....	85-94
Ore 5:	
Minus 10 mesh..	91-94
Pulverized.....	90-94

TABLE 4. - Sieve size distribution of ore sample 4, percent

Screen size, mesh	Minus 10 mesh	Pulverized
Plus 20.....	29	0
Minus 20 plus 35...	16	0
Minus 35 plus 65...	12	27
Minus 65 plus 100..	15	28
Minus 100 plus 200.	12	16
Minus 200 plus 325.	12	19
Minus 325.....	4	11

The number of residue washes also affected extraction. Table 5 shows the results of the washing tests. Residues were washed with a solution of equal volume and of similar composition to the leaching solution. Two washes were satisfactory for ore 5, which contained 0.78 pct WO_3, but three washes were required for ores 1 and 4, which contained 1.64 and 2.32 pct WO_3, respectively. A third wash increased extraction by 1.6 pct for ore 1 and by 6.1 pct for ore 4.

The CQL technique was applied to the five ores, using the best operating conditions, as described previously. Extraction results are shown in table 6. Tungsten extraction for four samples was near 90 pct. Extractions for ore 3 ranged from 73 to 82 pct.

TABLE 5. - Extraction of tungsten in pregnant and washing solutions, percent

Solutions	Ore 1[1]	Ore 4[2]	Ore 5[3]
Leach.....	52.5	50.7	53.4
Wash 1.....	35.8	28.0	24.3
Wash 2.....	2.3	8.0	7.7
Wash 3.....	1.6	6.1	.6
Wash 4.....	.5	.5	.6
Wash 5.....	.5	.5	.6
Total.....	93.2	93.8	87.2

[1] 1.64 pct WO_3.
[2] 2.32 pct WO_3.
[3] 0.78 pct WO_3.

TABLE 6. - Tungsten extraction from five ores

Ore	WO_3 in ore, pct	Tungsten extraction, pct
1	1.64	88-93
2	1.60	84-94
3	.68	73-82
4	2.32	85-94
5	.78	84-92

Five-Cycle Experiment

The CQL technique was investigated during a five-cycle experiment using ore 4, which contained 2.32 wt-pct WO_3. This experiment was performed to determine if the wash solutions could be added into the leach circuit to increase both the tungsten recovery and the tungsten content in the final pregnant solutions. Each cycle consisted of (1) calcining 2 kg of ore at 850° C for 3 hours in an oxidizing atmosphere, (2) quenching the hot calcine in 4 liters of solution containing 15 g/l NaOH and 15 g/l Na_2CO_3, (3) leaching the pulp at 200° C and 400 psig for 3 hours, and (4) filtering and washing the residue twice with 4,000 ml of solution containing 15 g/l Na_2CO_3 and 15 g/l NaOH. The wash solutions were reused in the succeeding cycles as shown in figure 5. The calcining and leaching

times were changed from 2 to 3 hours after the preliminary experimental results obtained with the 2-gal autoclave were evaluated.

The analyses of leaching and washing solutions and residues are shown in table 7. A material balance and the WO_3 and Na_2CO_3 distribution for the five cycles are shown in table 8. Tungsten extraction as calculated from the product analyses was 92.5 pct; as calculated from the head and residue analyses, it was 92.3 pct. The pregnant solutions contained 89.3 pct of the tungsten in the ore, and the fifth-cycle washing solutions contained 5.4 pct of the tungsten. Distribution shows 102 pct of the WO_3 was accounted for, but only 86 pct of the Na_2CO_3. The reason for the lower recovery of Na_2CO_3 has not been determined, but it was probably due to processing losses and the limit of analytical accuracy, since the values were based on the analysis of sodium.

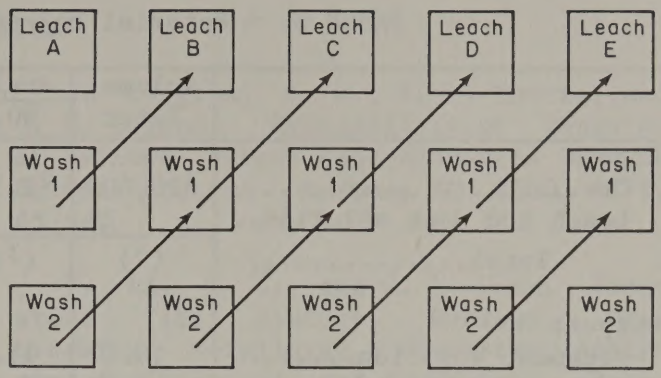

FIGURE 5. - Diagram of washing solutions progression.

TABLE 7. - Analyses of leaching and washing solutions and residues

	Volume, liters	WO_3, g/l	Na_2CO_3, g/l
Cycle A:			
Pregnant solution.....	4.050	8.7	20.7
Wash 1.....	4.060	1.9	27.6
Wash 2.....	3.950	.1	29.9
Residue.....	[1]1.600	[2].18	[2]3.23
Cycle B:			
Pregnant solution.....	3.580	10.9	22.4
Wash 1.....	4.000	2.8	29.9
Wash 2.....	3.900	.1	34.6
Residue.....	[1]1.717	[2].30	[2]2.76
Cycle C:			
Pregnant solution.....	3.580	12.6	21.8
Wash 1.....	3.920	3.2	29.9
Wash 2.....	3.980	.1	34.6
Residue.....	[1]1.650	[2].21	[2]2.3
Cycle D:			
Pregnant solution.....	3.920	11.5	19.5
Wash 1.....	3.960	2.8	29.9
Wash 2.....	3.940	.04	34.6
Residue.....	[1]1.628	[2].19	[2]3.0
Cycle E:			
Pregnant solution.....	3.740	11.5	20.7
Wash 1.....	3.860	3.2	29.9
Wash 2.....	3.920	.08	34.6
Residue.....	[1]1.629	[2].19	[2]2.76

[1]Grams. [2]Weight-percent.

TABLE 8. - Material balance for five-cycle experiment

	Volume, liter	Analysis, g/l		Weight, grams		Distribution, pct	
		WO_3	Na_2CO_3	WO_3	Na_2CO_3	WO_3	Na_2O_3
Input:							
Ore.....	[1]10,000	[2]2.32	[2]0.46	232	46	([3])	([3])
Leach and wash solution..	28	0	[4]35	0	980	([3])	([3])
Total.....	([3])	([3])	([3])	232	1,026	([3])	([3])
Output:							
Pregnant solution.....	18.87	11.0	21.0	207.2	395.7	89.3	38.6
Washing 1 solution.....	3.86	3.15	29.9	12.2	115.4	5.3	11.2
Washing 2 solution.....	3.92	.08	34.6	.3	135.6	.1	13.2
Residue.....	[1]8,224	[2].22	[2]2.8	17.7	230.9	7.6	22.5
Loss or gain[5].....	([3])	([3])	([3])	-5.4	148.4	-2.3	14.5
Total.....	([3])	([3])	([3])	232	1,026	100.0	100.0

[1]Grams.
[2]Weight-percent.
[3]Data entry not appropriate.
[4]15 g Na_2CO_3 + 15 g NaOH per liter converted to equivalent Na_2CO_3.
[5]Probably due to sampling and analytical errors.

DISCUSSION

In commercial processing, sodium tungstate solutions are treated to produce ammonium paratungstate (APT). Liquid ion-exchange extraction processes to produce APT from sodium tungstate solutions generated by alkaline digestion of tungsten ores are described by Yih and Wang (10) and Kurtak (5). The pregnant solutions contain impurities that must be reduced to acceptable levels before a crystallization operation to produce APT can be undertaken. The most frequently encountered contaminants are molybdenum, phosphorus, and silica.

The sodium tungstate solution generated by the five-cycle CQL experiment contained the following, in grams per liter:

WO_3.....	11.0
Na_2CO_3.....	21.0
Al_2O_3.....	.28
CaO.....	.028
Fe_2O_3.....	<.0002
MnO_2.....	<.0004
MoO_3.....	<.0004
P_2O_5.....	<.010
SiO_2.....	.20

The solution can be purified for crystallization to recover APT by the industrial practice described by Yih and Wang (10) and Kurtak (4-5).

SUMMARY AND CONCLUSIONS

The Golconda hot springs ores are not amenable to conventional beneficiation techniques. A hydrometallurgical procedure, the CQL technique, was developed to extract tungsten directly from the ores, and operating parameters were established. A tungsten extraction of 92 pct was obtained for one ore sample. Pregnant solutions containing 11 g/l WO_3 were produced.

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APPENDIX

Four ore samples were selected for the microprobe study: samples 2, 3, 4, and 5. These four were selected because they are representative of the major types of mineral assemblages in the deposit, and they include at least one sample from each of the three mine areas.

Representative samples were mounted in epoxy in 1-inch bakelite ring molds, ground and polished flat for microprobe examination and quantitative analysis at selected points. The instrument used was an International Scientific Instruments, Inc., Super IIIA scanning electron microscope, equipped with a Princeton Gamma Tech energy-dispersive X-ray spectrometer. Pieces of pure metals mounted and polished in the same manner as were the samples were used as compositional standards for the quantitative analysis.

Sample 2 from the Crib Shaft area contains 1.6 pct WO_3 and consists mainly of hydrated iron oxides, 29 pct; manganese oxides, 19 pct; and fluoride, 22 pct.

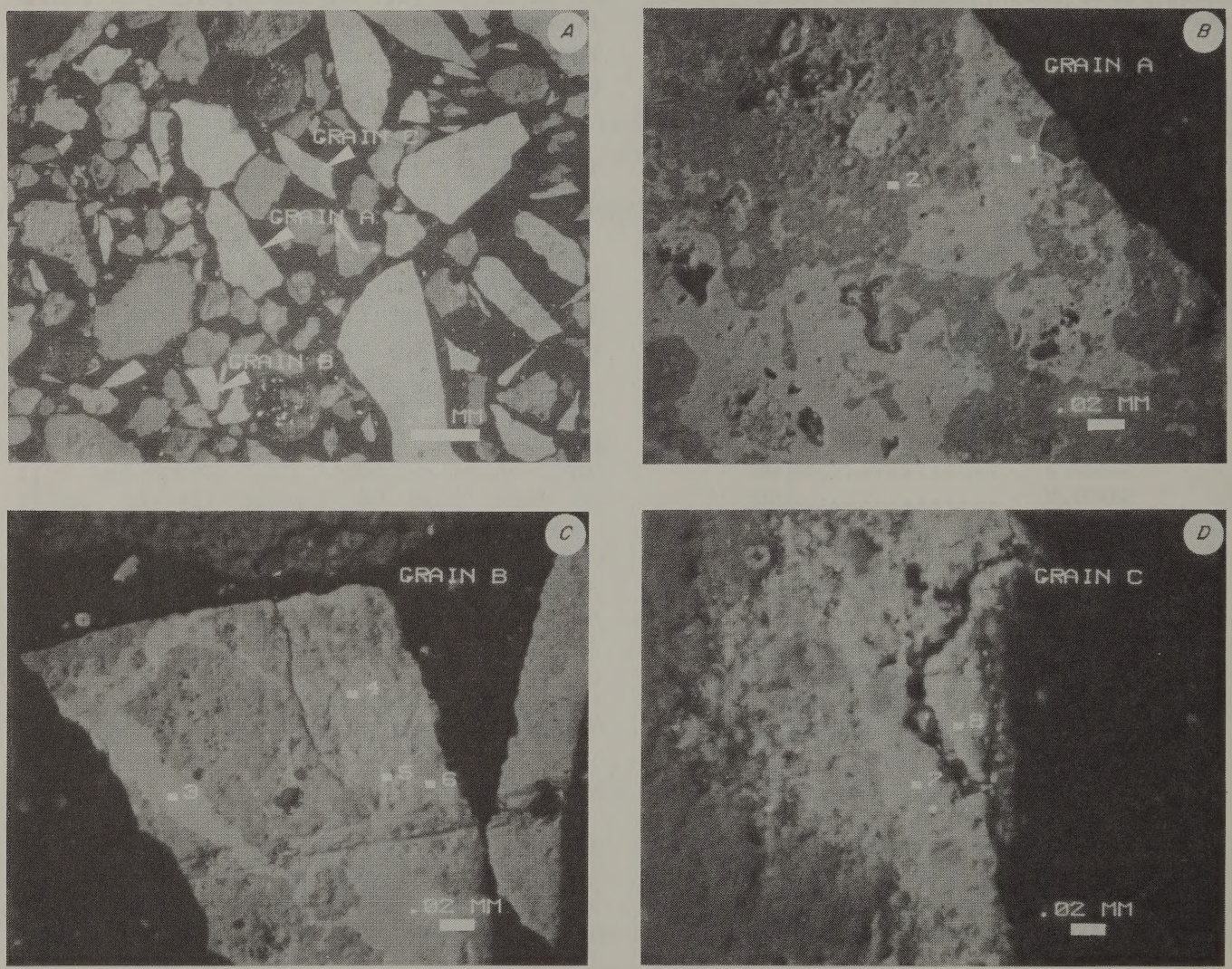

FIGURE A-1. - Scanning electron microscope photomicrographs taken in backscattered electron mode of sample 2 from Crib Shaft area. *A*, Typical grains; *B*, calcium-rich, iron-rich grain; *C*, complex manganese-iron oxide grains; *D*, iron oxide grain.

Kerr identified limonite as the major iron oxide mineral present in samples from this area (3). A polished section of the ground ore is shown in figure A-1A. The maximum dimensions of the grains range from 10 to 150 μm. The complex mineralogy of the ore is illustrated in figure A-1B. The high-calcium, dark material, probably fluorite, does not contain tungsten, while the high-iron, light material contains 2.7 pct W. Figure A-1C shows a grain composed of manganese oxide, lime-iron oxide mixture, and manganese-iron oxide mixture. The manganese oxide phase contains 58 pct Mn, 5.2 pct Ba, and 0.4 pct W. The lime-iron oxide phase contains 37 pct Ca, 10 pct Fe, 1.1 pct Ba, and 0.8 pct W. The manganese-iron oxide mixture contains 33 pct Mn, 17 pct Fe, 6.2 pct Ba, and 3.5 pct W. Figure A-1D shows a major iron oxide grain containing 51 pct Fe, 5.0 pct W, 0.3 pct Ba, and 0.2 pct Mn.

Analysis of the grains indicated by the points on the photomicrographs is shown in table A-1. In this ore, tungsten is associated with iron oxide grains containing <0.2 pct Mn and <0.6 pct Ba, and with manganese oxide grains containing 33 pct Mn, 6 to 17 pct Fe, and 6-7 pct Ba. Phases containing major quantities of calcium, 48 pct as limestone or fluorspar, have <0.1 pct W. Major calcium grains containing iron or manganese oxides analyzed up to 0.8 pct W.

TABLE A-1. - Microprobe analysis of ore sample 2, percent

Point[1]	W	Fe	Mn	Ba	Al	Ca	Si
1	2.7	54	0.4	0.4	1.4	1.3	2.4
2	0	2	0	.3	.5	48	1.1
3	.4	.3	58	5.2	.6	.8	.6
4	3.5	17	33	6.2	.5	.7	1.1
5	4.7	6	33	6.7	.6	4.6	3.0
6	.8	10	4	1.1	1.0	37	1.2
7	5.2	49	0	.2	1.8	.6	2.6
8	4.3	51	.2	.3	2.6	.6	3.1

[1]Points are shown on figure A-1.

Sample 3 containing 0.68 pct WO_3 is from the Bed Springs Hill area of the deposit. The sample consists mainly of ferric oxide and silica. A polished section of the sample is shown in figure A-2A. The ore contains some iron-rich grains without any tungsten, <0.1 pct Mn, and <0.3 pct Ba. Examples of these grains are shown in figure A-2B. Other grains with 30 to 40 pct Fe contain 16 pct Mn, 2 pct Ba, and 1.4 to 2.6 pct W. An example of the grains is shown in figure A-2C. A third high-manganese phase containing 6.6 to 7.6 pct W, 36 to 43 pct Mn, 8 to 10 pct Fe, and 6 to 7 pct Ba is shown in figure A-2D. Sample 3 contains only a minor quantity of manganese-rich grains and analyzed only 0.4 pct MnO_2.

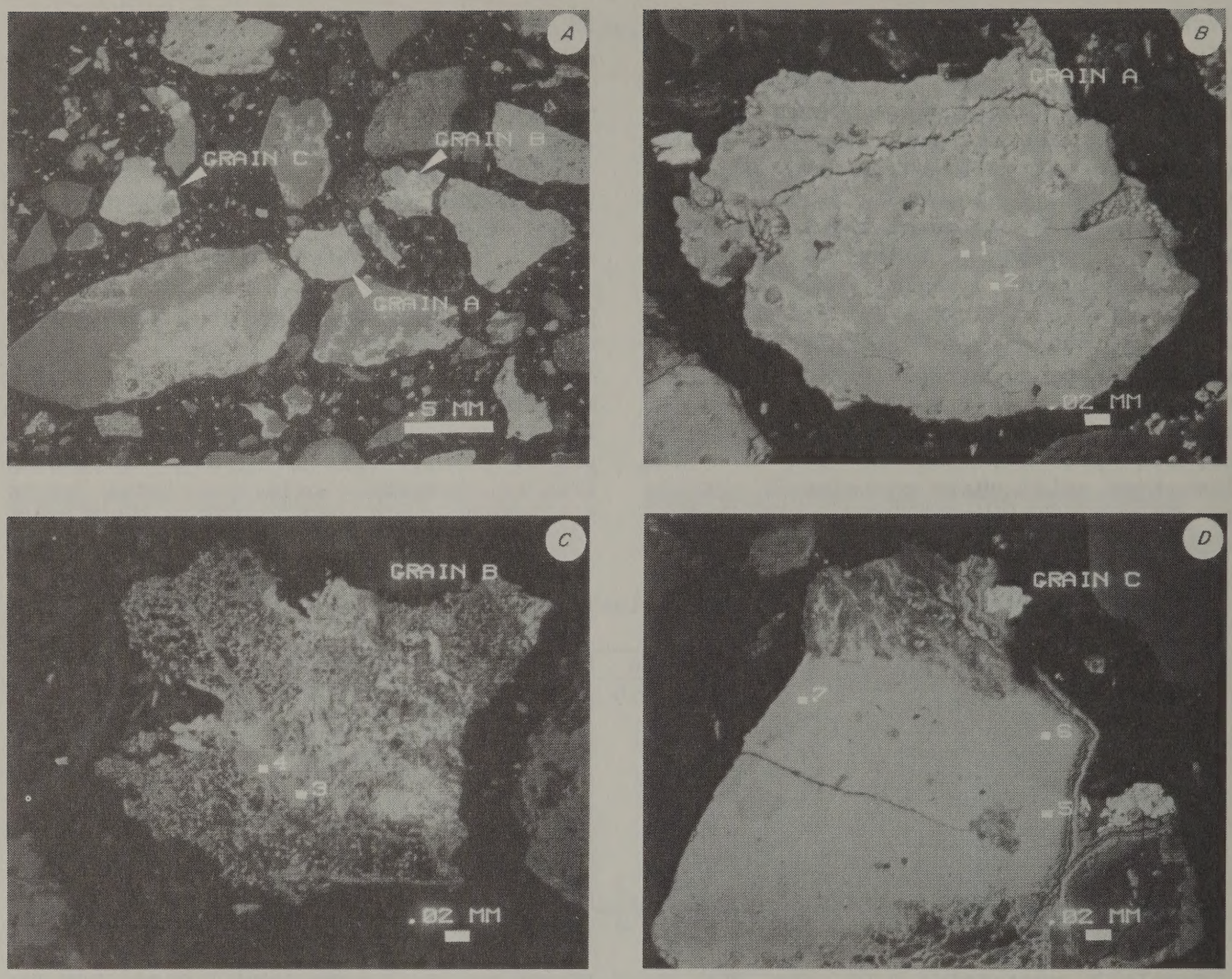

FIGURE A-2. - Scanning electron microscope photomicrographs taken in backscattered electron mode of sample 3 from Bed Springs Hill area. *A*, Typical grains; *B*, iron-rich grains; *C*, iron- and manganese-rich grains; *D*, manganese-rich grains.

In sample 3, the tungsten is associated with iron oxide phases containing both manganese and barium. Tungsten is not present in the iron oxide phases that contain <0.3 pct Ba and 0.1 pct Mn. The microprobe analysis of grains as indicated by the numbered points is shown in table A-2.

TABLE A-2. - Microprobe analysis of ore sample 3, percent

Point[1]	W	Fe	Mn	Ba	Al	Ca	Si
1	0	47	0	0.1	7.5	0.5	2.0
2	0	60	.1	.3	2.3	.3	2.0
3	2.6	40	16	2.2	2.3	.5	1.5
4	1.4	30	15	2.4	1.4	.5	10
5	6.6	2.6	43	7.6	.5	2.2	1.3
6	7.1	10	36	5.9	.8	2.0	1.2
7	7.6	8.2	36	6.4	.9	2.1	1.7

[1]Points are shown on figure A-2.

Sample 4 from the Big Four area of the mine is a high-grade ore containing 2.32 WO_3 and 69.4 pct manganese oxide. Kerr identified the major manganese minerals from this area as psilomelane and hollandite (3). Most of the grains contain >40 pct Mn, 4.4 to 5.5 pct W, 4.0 to 9.3 pct Ba, and <1.2 pct Fe. A typical grain is shown in figure A-3A. An iron-rich grain is shown in figure A-3B. The grain contains 47 pct Fe, 2.1 pct Mn, 0.6 pct Ba, and 3.3 pct W. Iron-rich grains are a minor constituent because sample 4 contains only 1.5 pct Fe. Figure A-3C shows an example of a complex grain with manganese-rich phases containing only 0.1 pct W intermixed with manganese-rich phases containing 4.8 pct W. The manganese-rich phases with only 0.1 pct W contain 20 pct silica, while the manganese-rich phases with 4.8 pct W contain only 3.5 pct silica. The analysis of grains indicated by the numbered points is shown in table A-3.

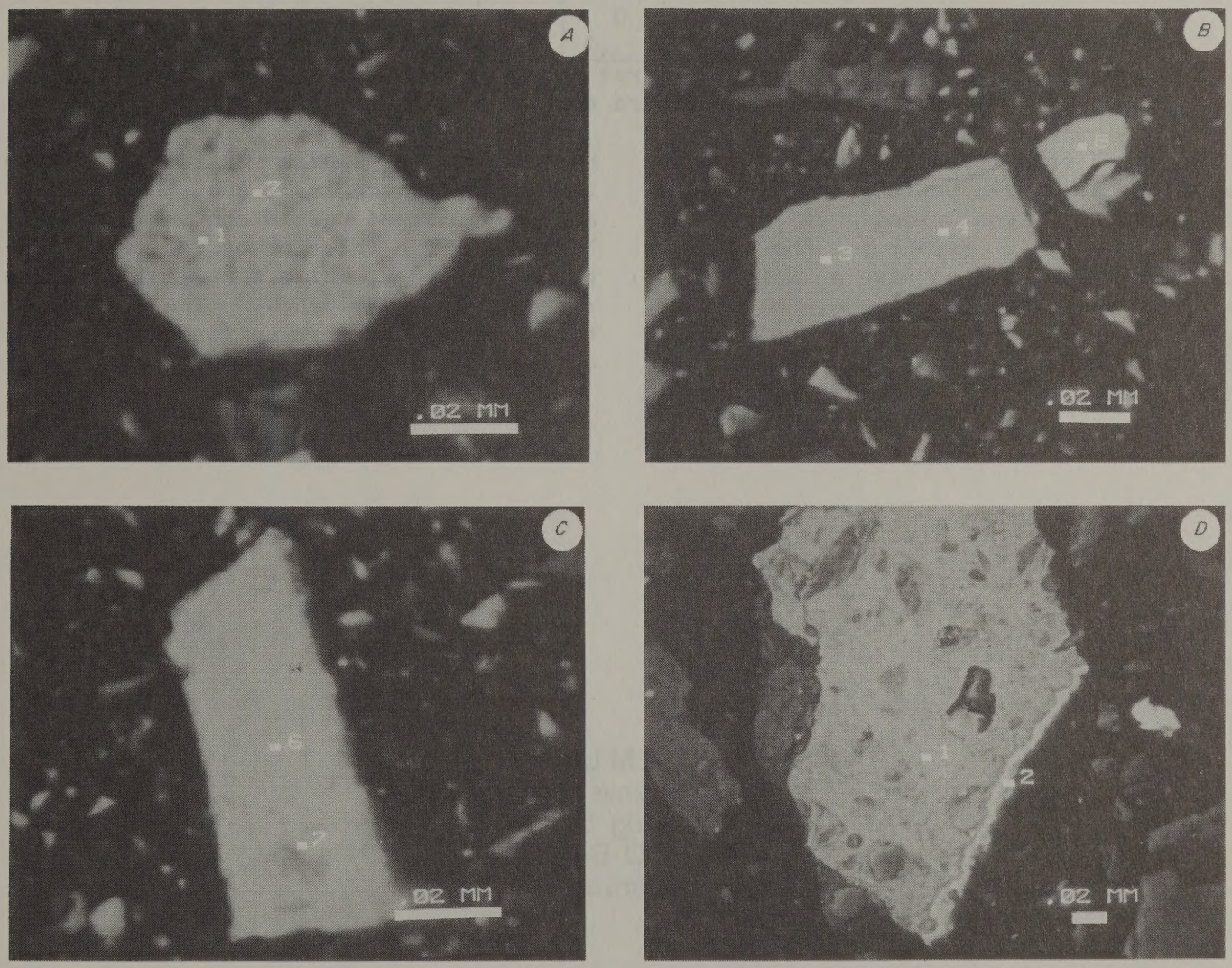

FIGURE A-3. - Scanning electron microscope photomicrographs taken in backscattered electron mode of samples 4 and 5 from Big Four area. *A*, Typical grain; *B*, iron-rich grains; *C*, manganese-rich grain; *D*, complex tungsten-containing grain.

TABLE A-3. - Microprobe analysis of ore samples 4 and 5, percent

Point	W	Fe	Mn	Ba	Al	Ca	Si
Sample 4:[1]							
1.....	4.4	0.4	49	6.3	0.5	2.2	1.4
2.....	5.5	.7	44	4.0	1.5	2.4	2.8
3.....	3.4	47	2.2	.7	1.8	.8	2.9
4.....	3.2	47	2.0	.5	1.7	.7	3.0
5.....	5.3	.8	46	4.3	.1	2.3	1.0
6.....	4.8	1.2	45	9.3	1.0	1.9	1.6
7.....	.1	.8	36	5.9	6.8	1.1	9.5
Sample 5:[2]							
1.....	2.2	45	0	.4	3.3	1.3	6.3
2.....	7.9	43	.2	.5	2.0	1.2	3.7

[1]Points are shown on figures A-3A, B, and C.
[2]Points are shown on figure A-3D.

Sample 5 from the Big Four area of the mine contains 0.78 pct WO_3 and is mainly composed of iron oxides, 24 pct, and silica, 44 pct. Except for the tungsten contents, the grains have a fairly consistent composition of iron, 44 to 52 pct, manganese, <0.2 pct, and barium, 0.2 to 0.7 pct. Tungsten contents range from 0 to 7.9 pct. The varying tungsten content in a single grain is illustrated in figure A-3D, and the analyses at the numbered points are shown in table A-3. The interior of the grain contains 2.2 pct W, while the veinlet on the rim contains 7.9 pct W. The grains in this ore had the most uniform composition of any of the ores examined.

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